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(54) Heat-sensitive imaging element for making positive working printing plates

(57) According to the present invention there is provided a heat-sensitive imaging element for making positive working lithographic printing plates comprising on a lithographic base a layer comprising a polymer, soluble in an aqueous alkaline solution and an IR-radiation sensitive top layer. Upon image-wise exposure the capacity of the aqueous alkaline solution to penetrate and/or solubilise the top layer is changed. Image-wise exposure can be performed with an infrared laser with a short as well as with a long pixel well time.

The obtained positive working printing plates have excellent printing properties and an improved infrared sensitivity.

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Description

1. Field of the invention.

The present invention relates to a heat-sensitive imaging element for making lithographic printing plates wherein the heat-sensitive imaging element comprises an IR-radiation sensitive top layer. The capacity of this top layer of being penetrated and/or solubilised by an aqueous developer is changed upon exposure.

2. Background of the invention.

Lithography is the process of printing from specially prepared surfaces, some areas of which are capable of accepting lithographic ink, whereas other areas, when moistened with water, will not accept the ink. The areas which accept ink form the printing image areas and the ink-rejecting areas form the background areas.

In the art of photolithography, a photographic material is made imagewise receptive to oily or greasy inks in the photo-exposed (negative-working) or in the non-exposed areas (positive-working) on a hydrophilic background.

In the production of common lithographic printing plates, also called surface litho plates or planographic printing plates, a support that has affinity to water or obtains such affinity by chemical treatment is coated with a thin layer of a photosensitive composition. Coatings for that purpose include light-sensitive polymer layers containing diazo compounds, dichromate-sensitized hydrophilic colloids and a large variety of synthetic photopolymers. Particularly diazo-sensitized systems are widely used.

Upon image-wise exposure of the light-sensitive layer the exposed image areas become insoluble and the unexposed areas remain soluble. The plate is then developed with a suitable liquid to remove the diazonium salt or diazo resin in the unexposed areas.

Alternatively, printing plates are known that include a photosensitive coating that upon image-wise exposure is rendered soluble at the exposed areas. Subsequent development then removes the exposed areas. A typical example of such photosensitive coating is a quinone-diazide based coating.

Typically, the above described photographic materials from which the printing plates are made are camera-exposed through a photographic film that contains the image that is to be reproduced in a lithographic printing process. Such method of working is cumbersome and labor intensive. However, on the other hand, the printing plates thus obtained are of superior lithographic quality.

Attempts have thus been made to eliminate the need for a photographic film in the above process and in particular to obtain a printing plate directly from computer data representing the image to be reproduced. However the photosensitive coating is not sensitive enough to be directly exposed with a laser. Therefor it has been proposed to coat a silver halide layer on top of the photosensitive coating. The silver halide can then directly be exposed by means of a laser under the control of a computer. Subsequently, the silver halide layer is developed leaving a silver image on top of the photosensitive coating. That silver image then serves as a mask in an overall exposure of the photosensitive coating. After the overall exposure the silver image is removed and the photosensitive coating is developed. Such method is disclosed in for example JP-A 60-61752 but has the disadvantage that a complex development and associated developing liquids are needed.

GB 1.492.070 discloses a method wherein a metal layer or a layer containing carbon black is provided on a photosensitive coating. This metal layer is then ablated by means of a laser so that an image mask on the photosensitive layer is obtained. The photosensitive layer is then overall exposed by UV-light through the image mask. After removal of the image mask, the photosensitive layer is developed to obtain a printing plate. This method however still has the disadvantage that the image mask has to be removed prior to development of the photosensitive layer by a cumbersome processing.

Furthermore methods are known for making printing plates involving the use of imaging elements that are heat-sensitive rather than photosensitive. A particular disadvantage of photosensitive imaging elements such as described above for making a printing plate is that they have to be shielded from the light. Furthermore they have a problem of sensitivity in view of the storage stability and they show a lower resolution. The trend towards heat-sensitive printing plate precursors is clearly seen on the market.

For example, Research Disclosure no. 33303 of January 1992 discloses a heat-sensitive imaging element comprising on a support a cross-linked hydrophilic layer containing thermoplastic polymer particles and an infrared absorbing pigment such as e.g. carbon black. By image-wise exposure to an infrared laser, the thermoplastic polymer particles are image-wise coagulated thereby rendering the surface of the imaging element at these areas ink-acceptant without any further development. A disadvantage of this method is that the printing plate obtained is easily damaged since the non-printing areas may become ink accepting when some pressure is applied thereto. Moreover, under critical conditions, the lithographic performance of such a printing plate may be poor and accordingly such printing plate has little lithographic printing latitude.

US-P-4,708,925 discloses imaging element including a photosensitive composition comprising an alkali-soluble novolac resin and an onium-salt. This composition can optionally contain an IR-sensitizer. After image-wise exposing said imaging element to UV - visible - or IR-radiation followed by a development step with an aqueous alkali liquid there is obtained a positive or negative working printing plate. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

EP-A-625728 discloses an imaging element comprising a layer which is sensitive to UV- and IR-irradiation and which can be positive or negative working. This layer comprises a resole resin,a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

US-P-5,340,699 is almost identical with EP-A-625728 but discloses the method for obtaining a negative working IR-laser recording imaging element. The IR-sensitive layer comprises a resole resin,a novolac resin, a latent Bronsted acid and an IR-absorbing substance. The printing results of a lithographic plate obtained by irradiating and developing said imaging element are poor.

Furthermore EP-A-678380 discloses a method wherein a protective layer is provided on a grained metal support underlying a laser-ablatable surface layer. Upon image-wise exposure the surface layer is fully ablated as well as some parts of the protective layer. The printing plate is then treated with a cleaning solution to remove the residu of the protective layer and thereby exposing the hydrophilic surface layer.

The above discussed systems have one or more disadvantages e.g. low infrared sensitivity, need for a pre-heating step (complex processing) or are not imageable at short as well as at long pixel dwell times. So there is still a need for heat-sensitive imaging materials that can be imaged by laser exposure at short as well as at long pixel dwell times and that yields lithographic printing plates with excellent printing properties.

3. Summary of the invention.

It is an object of the invention to provide a heat-sensitive imaging element for making lithographic printing plates having excellent printing properties, developable in a convenient ecological way.

It is further an object of the present invention to provide a heat-sensitive imaging element for making printing plates having a high infrared sensitivity.

It is also an object of the present invention to provide a heat-sensitive imaging element for making a printing plate of high quality which can be imaged by laser exposure at short as well as at long pixel dwell times.

Further objects of the present invention will become clear from the description hereinafter.

According to the present invention there is provided a heat-sensitive imaging element for making lithographic printing plates comprising on a lithographic base having a hydrophilic surface a hydrophobic layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation characterised in that said top layer upon exposure to IR-radiation has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution.

According to the present invention there is also provided a method for obtaining lithographic printing plates comprising the steps of image-wise exposing to IR-radiation a heat-sensitive imaging element as described above and developing said exposed imaging element by means of an aqueous alkaline solution. The pixel dwell time of the laser may be comprised between 0.005 μs and 20 μs.

4. Detailed description of the invention.

It has been found that according to the present invention, using a heat-sensitive imaging element as described above, lithographic printing plates of high quality can be obtained in an ecologically acceptable way.

A heat-sensitive imaging element in accordance with the present invention comprises on a lithographic base a hydrophobic layer comprising a polymer, soluble in an aqueous alkaline solution and an IR-radiation sensitive top layer.

The top layer, in accordance with the present invention comprises an IR-absorbing compound and a binder resin. Particularly useful IR-absorbing compounds are for example infrared dyes, metal carbides, borides, nitrides, carbonitrides, bronze-structured oxides and oxides structurally related to the bronze family but lacking the A component e.g. $WO_{2.9}$. Preferably carbon black is used as the IR-absorbing compound. As a binder resin gelatin, cellulose, cellulose esters e.g. cellulose acetate, polyvinyl alcohol, polyvinyl pyrrolidone, a copolymer of vinylidene chloride and acrylonitrile, poly(meth)acrylates, polyvinyl chloride, silicone resins etc. can be used. Preferred as binder resin is nitrocellulose.

In the top layer a difference in the capacity of being penetrated and/or solubilised by the aqueous alkaline solution is generated upon image-wise exposure. A difference in the capacity of the top layer to be penetrated and/or solubilised by a developing solution can be obtained by a thermally induced physical or chemical transformation. Examples of thermally induced physical transformations which generate a difference in said capacity are: laser induced coalescence of hydrophobic polymer particles in a hydrophilic binder as described in EP-A 952022871.0, 952022872.8, 952022873.6

and 952022874.4, which creates a reduction in the capacity of being penetrated and/or solubilised in the exposed areas and laser induced removal of material which creates an increase in the capacity in the exposed areas of the layer for penetration and/or solubilisation by the developing solution. Examples of thermally induced chemical transformations which generate a difference in the capacity of the layer for penetration and/or solubilisation by a developer are: laser induced change in polarity which increases the said capacity in the exposed areas and laser induced crosslinking which reduces the said capacity in the exposed areas. The change in said capacity created upon laser exposure, should be high enough to allow a complete clean-out without damaging and/or solubilising the resulting image upon development with an aqueous alkaline solution.

In thepreferred case that the said capacity is increased upon image-wise laser exposure, the imaged parts will be cleaned out during development without solubilising and/or damaging the non-imaged parts.

In the case that the said capacity is decreased upon image-wise laser exposure, the non-imaged parts will be cleaned out during development without solubilising and/or damaging the imaged parts.

The development with the aqueous alkaline solution is preferably done within an interval of 5 to 120 seconds.

In addition to the IR-sensitive compound the top layer may comprise a compound sensitive to visible light and/or UV-radiation to sensitise this layer to visible light and/or UV-radiation.

Between the top layer and the lithographic base the present invention comprises a hydrophobic layer soluble in an aqueous developing solution more preferably an aqueous alkaline developing solution with preferentially a pH between 7.5 and 14. The hydrophobic binders used in this layer are preferably hydrophobic binders as used in conventional positive or negative working PS-plates e.g. novolac, polyvinyl phenols, carboxy substituted polymers etc. Typical examples of these polymers are descibed in DE-A-4007428, DE-A-4027301 and DE-A-4445820. The hydrophobic binder used in connection with the present invention is further characterised by insolubility in water and partial solubility/swellability in an alkaline solution and/or partial solubility in water when combined with a cosolvent. Furthermore this aqueous alkali soluble layer is preferably a visible light- or UV-desensitised layer that is thermally hardenable and ink-accepting. This visible light- or UV-desensitised layer does not comprise photosensitive ingredients such as diazo compounds, photoacids, photoinitiators, quinone diazides, sensitisers etc. which absorb in the wavelength range of 250nm to 650nm. In this way a daylight stable printing plate can be obtained. Furthermore the IR-radiation sensitive top layer can be partially solubilised in the aqueous alkali soluble layer upon exposure.

In the imaging element according to the present invention, the lithographic base can be an anodised aluminum. A particularly preferred lithographic base is an electrochemically grained and anodised aluminum support. The anodised aluminum support may be treated to improve the hydrophilic properties of its surface. For example, the aluminum support may be silicated by treating its surface with sodium silicate solution at elevated temperature, e.g. 95°C. Alternatively, a phosphate treatment may be applied which involves treating the aluminum oxide surface with a phosphate solution that may further contain an inorganic fluoride. Further, the aluminum oxide surface may be rinsed with a citric acid or citrate solution. This treatment may be carried out at room temperature or can be carried out at a slightly elevated temperature of about 30 to 50°C. A further interesting treatment involves rinsing the aluminum oxide surface with a bicarbonate solution. It is further evident that one or more of these post treatments may be carried out alone or in combination. More detailed descriptions of these treatments are given in GB 1.084.070, DE-A-4423140, DE-A-4417907, EP-A-659909, EP-A-537633, DE-A-4001466,EP-A-292801, EP-A-291760 and US-P-4,458,005.

According to another embodiment in connection with the present invention, the lithographic base comprises a flexible support, such as e.g. paper or plastic film, provided with a cross-linked hydrophilic layer. A particularly suitable cross-linked hydrophilic layer may be obtained from a hydrophilic binder cross-linked with a cross-linking agent such as formaldehyde, glyoxal, polyisocyanate or a hydrolysed tetra-alkylorthosilicate. The latter is particularly preferred.

As hydrophilic binder there may be used hydrophilic (co)polymers such as for example, homopolymers and copolymers of vinyl alcohol, acrylamide, methylol acrylamide, methylol methacrylamide, acrylic acid, methacrylic acid, hydroxyethyl acrylate, hydroxyethyl methacrylate or maleic anhydride/vinylmethylether copolymers. The hydrophilicity of the (co)polymer or (co)polymer mixture used is preferably the same as or higher than the hydrophilicity of polyvinyl acetate hydrolyzed to at least an extent of 60 percent by weight, preferably 80 percent by weight.

The amount of crosslinking agent, in particular of tetraalkyl orthosilicate, is preferably at least 0.2 parts by weight per part by weight of hydrophilic binder, preferably between 0.5 and 5 parts by weight, more preferably between 1.0 parts by weight and 3 parts by weight.

A cross-linked hydrophilic layer in a lithographic base used in accordance with the present embodiment preferably also contains substances that increase the mechanical strength and the porosity of the layer. For this purpose colloidal silica may be used. The colloidal silica employed may be in the form of any commercially available water-dispersion of colloidal silica for example having an average particle size up to 40 nm, e.g. 20 nm. In addition inert particles of larger size than the colloidal silica can be added e.g. silica prepared according to Stöber as described in J. Colloid and Interface Sci., Vol. 26, 1968, pages 62 to 69 or alumina particles or particles having an average diameter of at least 100 nm which are particles of titanium dioxide or other heavy metal oxides. By incorporating these particles the surface of the cross-linked hydrophilic layer is given a uniform rough texture consisting of microscopic hills and valleys, which serve

as storag places for water in background areas.

The thickness of a cross-linked hydrophilic layer in a lithographic base in accordance with this embodiment may vary in the range of 0.2 to 25 μm and is preferably 1 to 10 μm.

Particular examples of suitable cross-linked hydrophilic layers for use in accordance with the present invention are disclosed in EP-A 601240, GB-P-1419512, FR-P-2300354, US-P-3971660, US-P-4284705 and EP-A 514490.

As flexible support of a lithographic base in connection with the present embodiment it is particularly preferred to use a plastic film e.g. substrated polyethylene terephthalate film, cellulose acetate film, polystyrene film, polycarbonate film etc... The plastic film support may be opaque or transparent.

It is particularly preferred to use a polyester film support to which an adhesion improving layer has been provided. Particularly suitable adhesion improving layers for use in accordance with the present invention comprise a hydrophilic binder and colloidal silica as disclosed in EP-A 619524, EP-A 620502 and EP-A 619525.

Preferably, the amount of silica in the adhesion improving layer is between 200 mg per m^2 and 750 mg per m^2. Further, the ratio of silica to hydrophilic binder is preferably more than 1 and the surface area of the colloidal silica is preferably at least 300 m^2 per gram, more preferably at least 500 m^2 per gram.

Image-wise exposure in connection with the present invention is an image-wise scanning exposure involving the use of a laser that operates in the infrared or near-infrared, i.e. wavelength range of 700-1500 nm. Most preferred are laser diodes emitting in the near-infrared. Exposure of the imaging element can be performed with lasers with a short as well as with lasers with a long pixel dwell time. Preferred are lasers with a pixel dwell time between 0.005 μs and 20 μs.

After the image-wise exposure the heat-sensitive imaging element is developed by rinsing it with an aqueous alkaline solution. The aqueous alkaline solutions used in the present invention are those that are used for developing conventional positive or negative working presensitised printing plates and have a pH between 7.5 and 14. Thus the imaged parts of the top layer that were rendered more penetrable for the aqueous alkaline solution upon exposure and the parts of the underlying layer are cleaned-out whereby a positive working printing plate is obtained. To obtain a negative working printing plate, the laser imaged parts of the layer are rendered less penetrable for the aqueous alkaline solution upon image-wise exposure, thus the non-imaged parts of the top layer and the parts of the underlying layer are cleaned out.

According to another embodiment of the method in accordance with the present invention the imaging element is first mounted on the printing cylinder of the printing press and then image-wise exposed directly on the press. Subsequent to exposure, the imaging element can be developed as described above.

The printing plate of the present invention can also be used in the printing process as a seamless sleeve printing plate. In this option the printing plate is soldered in a cylindrical form by means of a laser. This cylindrical printing plate which has as diameter the diameter of the print cylinder is slided on the print cylinder instead of applying in a classical way a classically formed printing plate. More details on sleeves are given in "Grafisch Nieuws" ed. Keesing, 15, 1995, page 4 to 6.

After the development of an image-wise exposed imaging element with an aqueous alkaline solution and drying, the obtained plate can be used as a printing plate as such. However, to improve durability it is still possible to bake said plate at a temperature between 200°C and 300°C for a period of 30 seconds to 5 minutes. Also the imaging element can be subjected to an overall post-exposure to UV-radiation to harden the image in order to increase the run lenght of the printing plate.

The following example illustrates the present invention without limiting it thereto. All parts and percentages are by weight unless otherwise specified.

EXAMPLES

Example 1 : Positive working thermal plate based on an alkali-soluble binder.
IR-laser exposure with short pixel dwell time(0.05μs)

Preparation of the lithographic base

A 0.20 mm thick aluminum foil was degreased by immersing the foil in an aqueous solution containing 5 g/l of sodium hydroxide at 50°C and rinsed with demineralized water. The foil was then electrochemically grained using an alternating current in an aqueous solution containing 4 g/l of hydrochloric acid, 4 g/l of hydroboric acid and 5 g/l of aluminum ions at a temperature of 35°C and a current density of 1200 A/m^2 to form a surface topography with an average center-line roughness Ra of 0.5 μm.
After rinsing with demineralized water the aluminum foil was then etched with an aqueous solution containing 300 g/l of sulfuric acid at 60°C for 180 seconds and rinsed with demineralized at 25°C for 30 seconds.
The foil was subsequently subjected to anodic oxidation in an aqueous solution containing 200 g/l of sulfuric acid at a

temperature of 45°C, a voltage of about 10 V and a current density of 150 A/m^2 for about 300 seconds to form an anodic oxidation film of 3.00 g/m^2 of Al_2O_3, th n washed with demineralized water, posttreated with a solution containing 20 g/l of sodium bicarbonate at 40°C for 30 seconds, subsequently rinsed with demineralized water at 20°C during 120 seconds and dried.

Preparation of the imaging element

On a lithographic base was first coated a 5 % by weight solution of MARUKA LYNCUR M H-2 (homopolymer of polyvinylphenol from Maruzen Co.) in methyl ethyl ketone to a wet thickness of 20 µm. This layer was dried for 10 minutes at 40°C.
Upon this layer was then coated, with a wet coating thickness of 20µm, the IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	579.7
Butylacetate	386.5
Special Schwarz 250 (carbon black available from Degussa)	16.7
Nitrocellulose E950 (available from Wolff Walsrode)	12.3
Solsperse 5000 (wetting agent available from ICI)	0.3
Solsperse 28000 (wetting agent available from ICI)	1.7
Cymel 301 (melamine hardener available from Dyno Cyanamid)	2.3
p-toluene sulfonic acid	0.5

The IR-sensitive coating was dried for 2 minutes at 120°C.

Imagewise exposure and processing of the imaging element

The IR-sensitive printing plate was subjected to a scannnig NdYAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05µs, spot size 14 µm and the power on the surface of the imaging element was varied from 2 Watts to 6 Watts). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (aqueous alkaline developing solution available from AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate.
After processing, the printing plate was mounted on a GTO46 offsetpress. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

Example 2 : Positive working thermal plate based on an alkali-soluble binder.
IR-laser exposure with long pixel dwell time (2.4µs)

The imaging element of example 1 was subjected to a scanning NdYlf-laser emitting at 1050 nm (scanspeed 4.4 m/s, pixel time 2.4 µs , spot size 15 µm and the power on plate surface was varied from 75 to 475 mW). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (aqueous alkaline developing solution available from AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate.
After processing, the printing plate was mounted on a GTO46 offsetpress. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

Example 3 : Positiv working thermal plate based on a thermally hardenable alkali-soluble layer composition.

Preparation of the lithographic base

see example 1

Preparation of the imaging element

On a lithographic base was first coated a 5 % by weight solution of a thermally hardenable composition in methyl ethyl ketone to a wet thickness of 20 μm. The resulting dry alkaline soluble, thermally hardenable layer had the following composition : 65 % w/w MARUKA LYNCUR M H-2 (homopolymer of polyvinylphenol from Maruzen Co.) , 30 % CYMEL 303 (hexamethoxymethyl melamine from Dyno Cyanamid), 5 % w/w TRIAZINE S (2,4,6-(trichloromethyl)-s-triazine from PCAS). This layer was dried for 10 minutes at 40°C.
Upon this layer was then coated, with a wet coating thickness of 20μm, the IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	579.7
Butylacetate	386.5
Special Schwarz 250 (carbon black available from Degussa)	16.7
Nitrocellulose E950 (available from Wolff Walsrode)	12.3
Solsperse 5000 (wetting agent available from ICI)	0.3
Solsperse 28000 (wetting agent available from ICI)	1.7
Cymel 301 (melamine hardener available from Dyno Cyanamid)	2.3
p-toluene sulfonic acid	0.5

The IR-sensitive coating was dried for 2 minutes at 120°C.

Imagewise exposure and processing of the imaging element

The IR-sensitive printing plate was subjected to a scannnig Nd YAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05μs, spot size 14 μm and the power on the surface of the imaging element was varied from 2 Watts to 6 Watts). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (aqueous alkaline developing solution available from AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate.
Then the resulting printing plate was post-baked for 2 minutes at 200°C to induce thermal hardening. This resulted in a printing plate with a higher run lenght compared to example 1.

Example 4 : Positive working thermal plate based on a UV-sensitive layer which is alkali-soluble.

Preparation of the imaging element

On an Ozasol N61 printing plate was coated an IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	579.7
Butylacetate	386.5
Special Schwarz 250 (carbon black available from Degussa)	16.7

(continued)

Nitrocellulose E950 (available from Wolff Walsrode)	12.3
Solsperse 5000 (wetting agent available from ICI)	0.3
Solsperse 28000 (wetting agent available from ICI)	1.7
Cymel 301 (melamine hardener available from Dyno Cyanamid)	2.3
p-toluene sulfonic acid	0.5

The UV-sensitive layer of the Ozasol N61 printing plate was coated by means of a knife coater with the IR-sensitive formulation to a wet coating thickness of 20 µm. The IR-sensitive coating was dried for 2 minutes at 120°C.

Imagewise exposure and processing of the imaging element

The IR-sensitive printing plate was subjected to a scannnig Nd YAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05µs, spot size 14 µm and the power on the surface of the imaging element was varied from 2 Watts to 6 Watts). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EN143 (developing solution available from AGFA), hereby removing the IR-imaged parts and resulting in a positive printing plate.
After processing, the printing plate was mounted on a GTO46 offsetpress. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

Example 5 : Positive working thermal plate based on an alkali-soluble binder.
IR-laser exposure with short pixel dwell time (0.05µs)

Preparation of the lithographic base

See example 1

Preparation of the imaging element

On a lithographic base was first coated a 5 % by weight solution of ALVONOL PN429 (cresol novolac from Hoechst) and 3,4,5-trimethoxybenzoic acid (from Aldrich) (ratio 88:12) in methyl ethyl ketone to a wet thickness of 20 µm. This layer was dried for 30 seconds at 120°C.
Upon this layer was then coated, with a wet coating thickness of 20µm, the IR-sensitive formulation on basis of a carbon black dispersion, with the following ingredients in parts by weight, as indicated.

Ethylacetate	900.0
Butylacetate	600.0
Special Schwarz 250 (carbon black available from Degussa)	22.0
Nitrocellulose E950 (available from Wolff Walsrode)	2.2
Solsperse 5000 (wetting agent available from ICI)	0.44
Solsperse 28000 (wetting agent available from ICI)	2.2

The IR-sensitive coating was dried for 30 seconds at 120°C.

Imagewise exposure and processing of the imaging element

The IR-sensitive printing plate was subjected to a scannnig NdYAG infrared laser emitting at 1064 nm in an internal drum configuration (scan speed 218 m/s, pixel time 0.05µs, spot size 14 µm and the power on the surface of the imag-

ing element was varied from 2 Watts to 6 Watts). After this exposure the IR-sensitive mask has partly disappeared in areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (aqueous alkaline developing solution available from AGFA) diluted with 10%, hereby removing the IR-imaged parts and resulting in a positive printing plate.
After processing, the printing plate was mounted on a GTO46 offsetpress. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

Example 6: Positive working thermal plate based on an alkali-soluble binder.
IR-laser exposure with long pixel dwell time (2.4μs).

The imaging element of example 5 was subjected to a scanning NdYlf-laser emitting at 1050 nm (scanspeed 4.4 m/s, pixel dwell 2.4μs, spot size 15μm and the power on the plate surface was varied from 75 to 475 mW). After this exposure the IR-sensitive mask has partly disappeared in the areas exposed to the laser-beam.
Further the imaging element was subjected to a developing process with Ozasol EP26 (aqueous alkaline developing solution available from AGFA) diluted with 10% water, hereby removing the IR-imaged parts and resulting in a positive printing plate.
After processing, the printing plate was mounted on a GTO46 offsetpress. As an ink was used K+E 123W and as a fountain solution Rotamatic. Printing was started and a good printing quality was obtained without any ink uptake in the IR-imaged parts.

Claims

1. A heat-sensitive imaging element for making a lithographic printing plate comprising on a lithographic base having a hydrophilic surface a hydrophobic layer comprising a polymer, soluble in an aqueous alkaline solution and a top layer that is sensitive to IR-radiation characterised in that said top layer upon image-wise IR-laser exposure has a decreased or increased capacity for being penetrated and/or solubilised by an aqueous alkaline solution.

2. A heat-sensitive imaging element according to claim 1 wherein said hydrophobic layer comprising a polymer is a visible light- or UV-desensitised layer.

3. A heat-sensitive imaging element according to claim 1 or 2 where upon image-wise laser exposure the capacity of the top layer to be penetrated and/or solubilised is increased, said increase leads to a clean-out of the laser imaged parts without solubilising and/or damaging the non-imaged parts upon developing said laser-imaged imaging element with an aqueous alkaline solution.

4. A heat-sensitive imaging element according to any of claims 1 or 2 wherein upon image-wise exposure the capacity of the top layer to be penetrated and/or solubilised is decreased, said decrease leads to a clean-out of the non-imaged parts without solubilising and/or damaging the laser imaged parts upon developing said laser exposed imaging element with an aqueous alkaline solution.

5. A heat-sensitive imaging element according to any of claims 1 to 4 wherein said hydrophobic layer soluble in an aqueous alkaline solution comprising a polymer is a thermally hardenable layer.

6. A heat-sensitive imaging element according to any of claims 1 to 5 wherein said hydrophobic layer soluble in an aqueous alkaline solution comprising a polymer comprises a hydrophobic binder.

7. A heat-sensitive imaging element according to any of claims 1 to 6 wherein said hydrophobic binder is characterised by insolubility in water and

    a. partial solubility or swellability in an aqueous alkaline solution and/or
    b. partial solubility in water when combined with a cosolvent

8. A heat-sensitive imaging element according to any of claims 1 to 7 wherein said hydrophobic binder is selected from the group consisting of novolacs, polyvinyl phenols, carboxy substituted polymers.

9. A heat-sensitive imaging element according to any of claims 1 to 8 wherein said IR-laser sensitive top layer com-

prises nitrocellulose.

10. A heat-sensitive imaging element according to any of claims 1 to 9 wherein said laser sensitive top layer comprises a light absorbing compound sensitive to:

- near IR-radiation and/or
- visible radiation and/or
- UV-radiation

11. A method for making lithographic printing plates comprising the steps of image-wise exposing a heat-sensitive imaging element comprising on a lithographic base having a hydrophilic surface, an aqueous alkaline soluble layer comprising a polymer and a top layer sensitive to IR-radiation and developing said imaging element.

12. A method according to claim 11 whereby the pixel dwell time of the laser is comprised between 0.005 μs and 20 μs.

13. A method according to any of claims 10 or 11 wherein said developing with an aqueous developing solution is done within an interval of 5 to 120 seconds.

14. A method according to any of claims 10 to 12 whereby the obtained printing plate is overall post-exposed to UV-radiation.

15. A method according to any of claims 10 or 13 wherein said aqueous developing solution is an aqueous alkaline solution with a pH between 7.5 and 14.

16. A method according to any of claims 10 to 14 whereby the obtained printing plate is post-baked in an additional step.

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EUROPEAN SEARCH REPORT

Application Number
EP 98 20 0496

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	EP 0 720 057 A (KONISHIROKU PHOTO IND) 3 July 1996 * page 33, line 35 - line 58 * * page 43, line 50 - page 44, line 10 * * page 47, line 29 - line 40 * * page 49, line 55 - page 50, line 22; claims 1,11; figure 1 *	1-12,15	B41C1/10 B41M5/36
P,X, L	EP 0 803 771 A (AGFA GEVAERT NV) 29 October 1997 * page 8, line 1 - line 8 * * page 10, line 44; claims; example 2 *	1,3-12	
P,X, L	EP 0 800 928 A (AGFA GEVAERT NV) 15 October 1997 * column 7, line 12 - line 40 *	1-12,15, 16	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			B41C B41M

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	15 July 1998	Philosoph, L

CATEGORY OF CITED DOCUMENTS

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(54) Title: HEAT-SENSITIVE COMPOSITION AND METHOD OF MAKING A LITHOGRAPHIC PRINTING FORM WITH IT

(57) Abstract

There is described coated on a lithographic base a complex of a developer-insoluble phenolic resin and a compound which forms a thermally frangible complex with the phenolic resin. This complex is less soluble in the developer solution than the uncomplexed phenolic resin. However when this complex is imagewise heated the complex breaks down so allowing the non-complexed phenolic resin to the dissolved in the developing solution. Thus the solubility differential between the heated areas of the phenolic resin and the unheated areas is increased when the phenolic resin is complexed. Preferably a laser-radiation absorbing material is also present on the lithographic base. A large number of compounds which form a thermally frangible complex with the phenolic resin have been located. Examples of such compounds are quinolinium compounds, benzothiazolium compounds, pyridinium compounds and imidazoline compounds.

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HEAT-SENSITIVE COMPOSITION AND METHOD OF MAKING A LITHOGRAPHIC PRINTING FORM WITH IT

This invention relates to positive working lithographic printing form precursors, to their use, and to imagable compositions for use thereon.

The art of lithographic printing is based on the immiscibility of oil and water, wherein the oily material or ink is preferentially retained by the image area and the water or fountain solution is preferentially retained by the non-image area. When a suitably prepared surface is moistened with water and an ink is then applied, the background or non-image area retains the water while the image area accepts ink and repels the water. The ink on the image area is then transferred to the surface of a material upon which the image is to be reproduced, such as paper, cloth and the like. Commonly the ink is transferred to an intermediate material called the blanket which in turn transfers the ink to the surface of the material upon which the image is reproduced.

A generally used type of lithographic printing form precursor has a light sensitive coating applied to an aluminium base support. Negative working lithographic printing form precursors have a radiation sensitive coating which when imagewise exposed to light hardens in the exposed areas. On development the non-exposed areas of the coated composition are removed leaving the image. On the other hand positive working lithographic printing form precursors have a coated composition, which after imagewise exposure to light of an appropriate wavelength, becomes more soluble in the exposed areas than in the non-exposed areas in a developer. This light induced solubility differential is called photosolubilisation. A large number of commercially available positive working printing form precursors coated with quinone diazides together with a phenolic resin work by photosolubilisation to produce an image. In both cases the image area on the printing form itself is ink-receptive or oleophilic and the non-image area or background is water receptive or hydrophilic.

The differentiation between image and non-image areas is made in the exposure process where a film is applied to the printing form precursor with a vacuum to ensure good contact. The printing form precursor is then exposed to a light source, a portion of which is composed of UV radiation. In the instance where a positive printing form precursor is used, the area of

the film that corresponds to the image on the printing form precursor is opaque so that no light will strike the printing form precursor, whereas the area on the film that corresponds to the non-image area is clear and permits the transmission of light to the coating which becomes more soluble and is removed.

More recent developments in the field of lithographic printing form precursors have provided radiation-sensitive compositions useful for the preparation of direct laser addressable printing form precursors. Digital imaging information can be used to image the printing form precursor without the need to utilise an imaging master such as a photographic transparency.

An example of a positive working, direct laser addressable printing form precursor is described in US 4,708,925, issued November 24th 1987. This patent describes a lithographic printing form precursor in which the imaging layer comprises a phenolic resin and a radiation-sensitive onium salt. As described in the patent, the interaction of the phenolic resin and the onium salt produces an alkali-insoluble composition which is restored to alkali solubility upon photolytic decomposition of the onium salt. The printing form precursor can be utilised as a positive working printing form precursor or as a negative working printing form precursor using additional process steps between exposure and development as detailed in British Patent no. 2,082,339. The printing form precursors described in US 4,708,925 are intrinsically sensitive to UV radiation and can be additionally sensitised to visible and infra-red radiation.

A further example of a laser addressable printing form precursor which can be utilised as a direct positive working system is described in US 5,372,907, issued December 13th 1994, and US 5,491,046, issued February 13th 1996. These two patents describe a radiation induced decomposition of a latent Bronsted acid to increase the solubility of the resin matrix on imagewise exposure. As with the printing form precursor described in US 4,708,925 these systems can be additionally utilised as a negative working system with additional process steps after imaging and pre-development. In the negative working process the decomposition by-products are subsequently used to catalyse a cross-linking reaction between resins to insolubilise the imaged areas prior to development. As in US 4,708,925 these printing form precursors are intrinsically sensitive to UV radiation due to the acid generator materials used.

The hereinabove described printing form precursors of the prior art which can be employed as direct imaged positive working printing form precursors are lacking in one or more desirable features. None of the printing form precursors described can be handled extensively without due consideration for the lighting conditions in the working area. In order to handle the printing form precursors for unlimited periods special safelighting conditions are required which prevent unwanted exposure to UV radiation. The printing form precursors may be utilised for limited periods only in white light working conditions dependent on the output spectrum of the white light source. It would be desirable to utilise digital imaging hardware and printing form precursors in the unrestricted, white light press room environment in order to streamline workflows and UV sensitivity would be a disadvantage in these areas. In addition, white light handling would provide an improved working environment in traditional pre-press areas which currently have to be under restrictive safelight conditions.

Moreover, both printing form precursor systems have constraints on their components which create difficulties in optimising plate properties to provide optimum performance across the wide range of demanding lithographic plate performance parameters, including developer solubility, ink receptivity, runlength, adhesion.

In the systems described in US 4,708,925 the presence of functional groups which would crosslink the phenolic resin in the presence of the onium salts upon irradiation cannot be allowed, either as a modification to the alkali soluble resin or as additional components in the composition, as this would lead to reduced solubilisation on exposure.

An essential requirement of the compositions described in US 5,491,046 is the presence of both a resole resin and a novolak resin in order to allow the use of the system in a negative working mode. This is the favoured mode for this system as demonstrated by the negative working patent examples and the first commercialised product derived from this proprietary technology, Kodak's Performer product. This optimisation for negative working potential restricts optimisation for the positive working mode which does not have this requirement.

A wide range of heat solubilising compositions useful as thermographic recording materials have previously been disclosed in GB 1,245,924, issued September 15th 1971, such that the solubility of any given area of the imagable layer in a given solvent can be increased by the heating of the layer by indirect exposure to a short duration high intensity visible light and/or infrared radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material. The systems described are varied and operate by many different mechanisms and use different developing materials ranging from water to chlorinated organic solvents. Included in the range of compositions disclosed which are aqueous developable are those which comprise a novolak type phenolic resin. The patent suggests that coated films comprising of such resins will show increased solubility on heating. The compositions may contain heat absorbing compounds such as carbon black or Milori Blue (C.I. Pigment Blue 27). These materials additionally colour the images for their use as a recording medium.

The level of solubility differential in the compositions described in GB 1,245,924, however, is very low compared to that of commercial positive working lithographic printing form precursor compositions. Standard lithographic printing form precursors are able to demonstrate excellent tolerance to strong developing solutions, good robustness to variations in customer use and can be optimised to provide high developer solution usage and high numbers of printed impressions. The very poor developer latitude exhibited by the compositions of GB 1,245,924 makes them unsuitable for commercially acceptable lithographic printing form precursors.

We have discovered a heat-sensitive composition suitable for application as a heat-sensitive positive working printing form precursor for heat mode imaging which does not exhibit the disadvantages of the prior art as described hereinabove.

The composition of the present invention is heat-sensitive in that localised heating of the composition, preferably by suitable radiation, causes an increase in the aqueous developer solubility of the exposed areas.

Therefore according to one aspect of the present invention there is provided an oleophilic, heat-sensitive composition comprising an aqueous developer soluble polymeric substance, hereinafter called the "active polymer", and a compound which reduces the aqueous developer solubility of the polymeric substance, hereinafter called the "reversible insolubiliser compound", characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

According to a further aspect of the present invention there is provided a positive working lithographic printing form precursor having a coating comprising of a composition comprising a said active polymer and a said reversible insolubiliser compound coated on a support having a hydrophilic surface characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

In order to increase the sensitivity of the heat-sensitive compositions of the present invention it is beneficial to include an additional component, namely a radiation absorbing compound capable of absorbing incident radiation and converting it to heat, hereinafter called a "radiation absorbing compound".

Therefore a further aspect of the present invention is a lithographic printing form precursor wherein said coating is suitably adapted to preferentially absorb radiation and convert said radiation to heat.

Therefore according to a preferred embodiment of the present invention there is provided a heat-sensitive positive working lithographic printing form precursor which has on a support having a hydrophilic surface an oleophilic, heat-sensitive composition comprising a said active polymer, a said reversible insolubiliser compound and a said radiation absorbing compound, characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

In a further preferred embodiment of the present invention there is provided a heat-sensitive positive working lithographic printing form precursor wherein the said coating includes an additional layer disposed beneath the oleophilic, heat-sensitive composition, wherein the additional layer comprises a radiation absorbing compound.

In a further preferred embodiment of the present invention there is provided a heat-sensitive positive working lithographic printing form precursor which has on a support having a hydrophilic surface an oleophilic, heat-sensitive composition comprising a said active polymer and a said reversible insolubiliser compound which is also a said radiation absorbing compound characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

In the specification, when we state that the aqueous developer solubility of the composition is increased on heating we mean that it is substantially increased, i.e. by an amount useful in a lithographic printing process. When we state that the aqueous developer solubility of the composition is not increased by incident UV radiation we mean that it is not substantially increased, that is by an amount which would mean that UV safelighting conditions would have to be employed. Thus, insubstantial increases in solubility on UV radiation may be tolerated within the scope of this invention.

The printing form is preferably a lithographic plate and will be referred to as such hereinafter.

Thus in all preferred embodiments of the present invention a positive working lithographic printing plate is obtained after heat-mode imaging and processing. The aqueous developer solubility of the coated composition is much reduced with respect to the solubility of the active polymer alone. On subsequent exposure to suitable radiation the heated areas of the composition are rendered more soluble in the developing solution. Therefore on imagewise exposure there is a change in the solubility differential of the unexposed composition and of the exposed composition. Thus in the exposed areas the composition is dissolved revealing the underlying hydrophilic surface of the plate.

The coated plates of the invention may be heat imaged indirectly by exposure to a short duration of high intensity radiation transmitted or reflected from the background areas of a graphic original located in contact with the recording material.

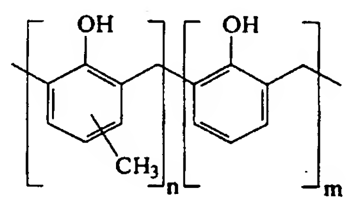
In another aspect of the invention preferably the plates may be imagewise heated using a heated body. For example, the plates, either the reverse face or, preferably, the heat sensitive composition, may be contacted by heat stylus.

In another aspect of the invention preferably the plate is exposed directly by means of a laser to heat the coating imagewise. Most preferably the laser emits radiation at above 600nm.

Whilst the applicants do not wish to be limited by any theoretical explanation of how their invention operates, it is believed that a thermally frangible complex is formed between the active polymer and the reversible insolubiliser compound. This complex is believed to be reversibly formed and can be broken by application of heat to the complex to restore aqueous developer solubility to the composition. It is thought that polymeric substances suitable for use in the current invention comprise electron rich functional groups when uncomplexed and that suitable compounds which reduce the aqueous developer solubility of the polymeric substance are electron poor. It is not thought that decomposition of components within the composition is required, or that any substantial decomposition has occurred in any examples tested to date.

Examples of functional groups of said active polymers suitable for application in this invention include hydroxy, carboxylic acid, amino, amide and maleiimide functional groups. A wide range of polymeric materials are suitable for use in the present invention examples of which include phenolic resins; copolymers of 4-hydroxystyrene, for example with 3-methyl-4-hydroxystyrene or 4-methoxystyrene; copolymers of (meth)acrylic acid, for example with styrene; copolymers of maleiimide, for example with styrene; hydroxy or carboxy functionalised celluloses; copolymers of maleic anhydride, for example with styrene; partially hydrolysed polymers of maleic anhydride.

Most preferably the active polymer is a phenolic resin. Particularly useful phenolic resins in this invention are the condensation products from the interaction between phenol, *C*-alkyl substituted phenols (such as cresols and p-tert-butyl-phenol), diphenols (such as bisphenol-A) and aldehydes (such as formaldehyde). Dependent on the preparation route for the condensation a range of phenolic materials with varying structures and properties can be formed. Particularly useful in this invention are novolak resins, resole resins and novolak/resole resin mixtures. Examples of suitable novolak resins have the following general structure.



A large number of compounds which reduce the aqueous solubility of suitable polymeric substances have been located for use as reversible insolubiliser compounds.

A useful class of reversible insolubiliser compounds are nitrogen containing compounds wherein a least one nitrogen atom is either quarternised, incorporated in a heterocyclic ring or quarternised and incorporated in a heterocyclic ring.

Examples of useful quaternised nitrogen containing compounds are triaryl methane dyes such as Crystal Violet (CI basic violet 3) and Ethyl Violet and tetraalkyl ammonium compounds such as Cetrimide.

More preferably the reversible insolubiliser compound is a nitrogen-containing heterocyclic compound.

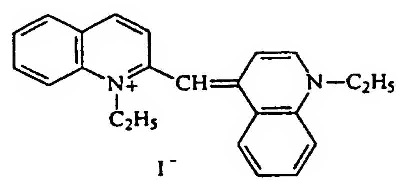
Examples of suitable nitrogen-containing heterocyclic compounds are quinoline and triazols, such as 1,2,4-triazol.

Most preferably the reversible insolubiliser compound is a quarternised heterocyclic compound.

Examples of suitable quarternised heterocyclic compounds are imidazoline compounds, such as Monazoline C, Monazoline 0, Monazoline CY and Monazoline T all of which are manufactured by Mona Industries, quinolinium compounds, such 1-ethyl-2-methyl quinolinium iodide and 1-ethyl-4-methyl quinolinium iodide, and benzothiazolium compounds, such as 3-ethyl-2-methyl benzothiazolium iodide, and pyridinium compounds, such as cetyl pyridinium bromide, ethyl viologen dibromide and fluoropyridinium tetrafluoroborate.

Usefully the quinolinium or benzothiazolium compounds are cationic cyanine dyes, such as Dye A, Quinoldine Blue and 3-ethyl-2-[3-(3-ethyl-2(3H)-benzothiazolylidene)-2-methyl-1-propenyl] benzothiazolium iodide.

Dye A



A further useful class of reversible insolubiliser compounds are carbonyl functional group containing compounds.

Examples of suitable carbonyl containing compounds are α-naphthoflavone, β-naphthoflavone, 2,3-diphenyl-1-indeneone, flavone, flavanone, xanthone, benzophenone, N-(4-bromobutyl)phthalimide and phenanthrenequinone.

The reversibly insolubilising compound may be a compound of general formula

$$Q_1\text{-}S(O)_n\text{-}Q_2$$

Where Q_1 represents an optionally substituted phenyl or alkyl group, n represents 0, 1 or 2, and Q_2 represents a halogen atom or an alkoxy group. Preferably Q_1 represents a C_{1-4} alkyl

phenyl group, for example a tolyl group, or a C_{1-4} alkyl group. Preferably n represents 1 or, especially, 2. Preferably Q_2 represents a chlorine atom or a C_{1-4} alkoxy group, especially an ethoxy group.

Another useful reversible insolubiliser compound is acridine orange base (CI solvent orange 15).

Other useful reversible insolubiliser compounds are ferrocenium compounds, such as ferrocenium hexafluorophosphate.

In addition to the active polymer which interacts with the reversible insolubiliser compound in the manner defined herein the composition may contain a polymeric substance which does not thus interact. In such a composition having a blend of polymeric substances it should be noted that the active polymer can be present in a lower amount, by weight, than the additional polymeric substance(s). Suitably the active polymer is present in an amount of at least 10%, preferably at least 25%, more preferably at least 50%, by total weight of the polymer substances present in the composition. Most preferably, however, the active polymer is present to the exclusion of any polymeric substance which does not thus interact.

The major proportion of the composition is preferably constituted by polymeric substance(s), including the active polymer and, when present, an additional polymeric substance which does not thus interact. Preferably a minor proportion of the composition is constituted by the reversible insolubiliser compound.

A major proportion as defined herein is suitably at least 50%, preferably at least 65%, most preferably at least 80%, of the total weight of the composition,

A minor proportion as defined herein is suitably less than 50%, preferably up to 20%, most preferably up to 15%, of the total weight of the composition.

Suitably the reversible insolubiliser compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15% of the total weight of the composition.

Thus a preferred weight range for the reversible insolubiliser compound may be expressed as 2-15% of the total weight of the composition.

There may be more than one polymeric substance which interacts with the said compound. References herein to the proportion of such substance(s) are to their total content. Likewise there may be more than one polymeric substance which does not thus interact. References herein to the proportion of such substance(s) are to their total content. Likewise there may be more than one reversible insolubiliser compound. References herein to the proportion of such compound(s) are to their total content.

The aqueous developer composition is dependent on the nature of the polymeric substance. Common components of aqueous lithographic developers are surfactants, chelating agents such as salts of ethylenediamine tetraacetic acid, organic solvents such as benzyl alcohol, and alkaline components such as inorganic metasilicates, organic metasilicates, hydroxides or bicarbonates.

Preferably the aqueous developer is an alkaline developer containing inorganic or organic metasilicates when the polymeric substance is a phenolic resin.

Six simple tests, tests 1 to 6, may be carried out to determine if the composition comprising the active polymer and the reversible insolubiliser compound and a suitable aqueous developer are suitable for use in the present invention.

Test 1. The composition comprising the active polymer in the absence of the reversible insolubiliser compound is coated on a hydrophilic support and dried. Then the surface is inked-up. If a uniform inked coating is obtained then the composition is oleophilic when laid down as a layer.

Test 2. The hydrophilic support coated with the composition comprising the active polymer in the absence of the reversible insolubiliser compound is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be between 30 to 60 seconds, at room temperature, and then rinsed,

dried and inked-up. If no ink surface is obtained then the composition has dissolved in the developer.

Test 3. The composition comprising the active polymer and the reversible insolubiliser compound is coated on a hydrophilic support, dried and inked-up. If a uniform inked coating is obtained then the composition is oleophilic when laid down as a layer

Test 4. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be between 30 and 60 seconds, at room temperature, and then rinsed, dried and inked-up. If a uniform inked coating is obtained then the composition does not substantially dissolve in the developing solution.

Test 5. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a suitable temperature for an appropriate time. Then it is processed in a suitable aqueous developer for a reasonable period of time at room temperature.

The surface is then dried and inked-up. If no ink surface is obtained then the heated composition has dissolved in the developer.

The temperature and time depend on the components selected for the composition and on their proportion. Simple trial and error experiments may be undertaken to determine suitable conditions. If such experiments cannot yield conditions which allow the test to be passed, the conclusion must be that the composition does not pass this test.

Preferably, for typical compositions, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 160°C for 5 to 20 seconds. Then it is

processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be 30 to 120 seconds, at room temperature.

Most preferably, the composition comprising the active polymer and the reversible insolubiliser compound is heated in an oven such that the composition reaches a temperature of 50°C to 120°C for 10 to 15 seconds. Then it is processed in a suitable aqueous developer for 30 to 90 seconds at room temperature.

Test 6. The hydrophilic support coated with the composition comprising the active polymer and the reversible insolubiliser compound is exposed to U.V. light for a suitable time which may be determined by trial and error but will typically be 30 seconds. Then it is processed in a suitable aqueous developer for a suitable time which may be determined by trial and error but will typically be 30 to 60 seconds at room temperature. The surface is then dried and inked-up. If the coating is inked-up no UV radiation induced solubilisation of the composition has occurred and thus the composition is suitably robust to normal working lighting conditions.

If the composition can pass all six tests then it is suitable for use in the present invention.

A large number of compounds, or combinations thereof, can be utilised as radiation absorbing compounds in preferred embodiments of the present invention.

In preferred embodiments the radiation absorbing compound absorbs infra-red radiation. However, other materials which absorb other wavelength radiation (excluding UV wavelengths), e.g. 488 nm radiation from an Ar-ion laser source, may be used with the radiation being converted to heat.

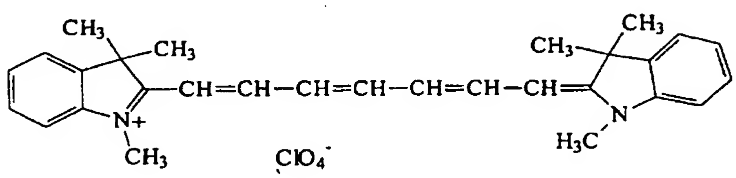
The radiation absorbing compound is usefully carbon such as carbon black or graphite. It may be a commercially available pigment such as Heliogen Green as supplied by BASF or

Nigrosine Base NG1 as supplied by NH Laboratories Inc or Milori Blue (C.I. Pigment Blue 27) as supplied by Aldrich.

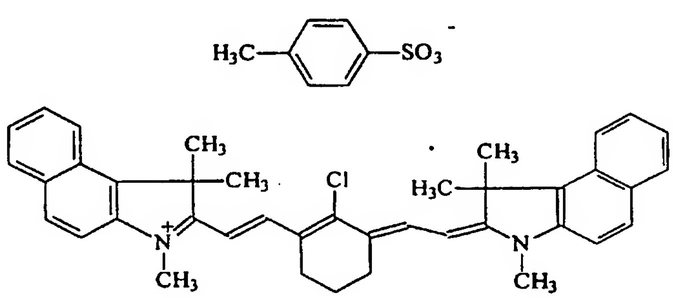
In a preferred method of the invention the coated plate is imagewise exposed directly by a laser. Most preferably the laser emits radiation at above 600nm and the radiation absorbing compound is usefully an infra-red absorbing dye.

Preferably the infra-red absorbing compound is one whose absorption spectrum is significant at the wavelength output of the laser which is to be used in the method of the present invention. Usefully it may be an organic pigment or dye such as phthalocyanine pigment. Or it may be a dye or pigment of the squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline classes.

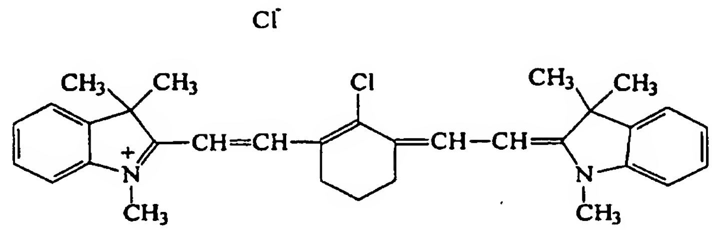
Examples of such compounds are:-



and Dye B



and Dye C, KF654 B PINA as supplied by Riedel de Haen UK, Middlesex, England, believed to have the structure:



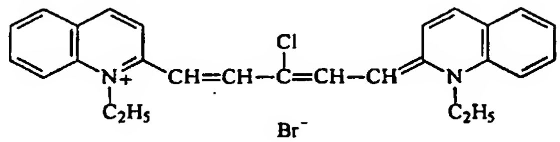
Suitably the radiation absorbing compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15%, of the total weight of the composition. Thus a preferred weight range for the radiation absorbing compound may be expressed as 2-15% of the total weight of the composition. Likewise there may be more than one radiation absorbing compound. References herein to the proportion of such compound(s) are to their total content.

In one preferred embodiment of the invention an additional layer comprising a radiation absorbing compound can be used. This multiple layer construction can provide routes to high sensitivity as larger quantities of absorber can be used without affecting the function of the imaging forming layer. In principle any radiation absorbing material which absorbs sufficiently strongly in the desired wavelength range can be incorporated or fabricated in a uniform coating. Dyes, metals and pigments (including metal oxides) may be used in the form of vapour deposited layers, techniques for forming and use of such films are well known in the art, for example in EP 0,652,483. The preferred components in the present invention are those that are hydrophilic as the uniform coating or which can be treated to provide a hydrophilic surface, for example by use of a hydrophilic layer.

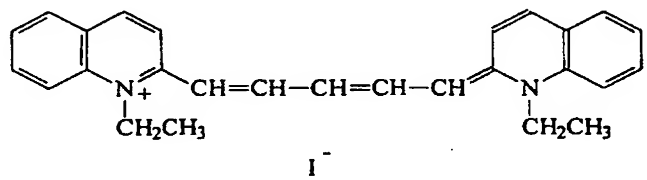
Compounds which reduce the aqueous developer solubility of the polymeric substance and are also radiation absorbing compounds suitable for one embodiment of the present invention are preferably cyanine dyes and most preferably quinolinium cyanine dyes which absorb at above 600nm.

Examples of such compounds are:-

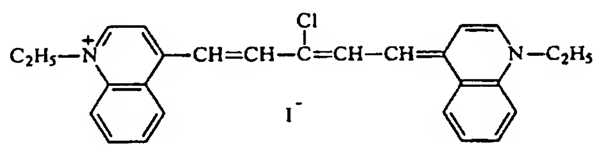
2-[3-chloro-5-(1-ethyl-2(1H)-quinolinylidene)-1,3-pentadienyl]-1-ethylquinolinium bromide



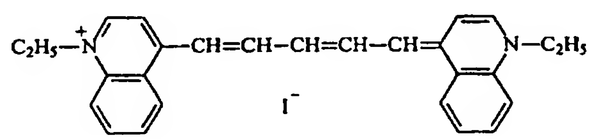
1-Ethyl-2-[5-(1-ethyl-2(1H)-quinolinylidene)-1,3-pentadienyl] quinolinium iodide



4-[3-chloro-5-(1-ethyl-4(1H)-quinolinylidene)-1,3-pentadienyl]-1-ethylquinolinium iodide



Dye D, 1-Ethyl-4-[5-(1-ethyl-4(1H)-quinolinylidene)-1,3-pentadienyl] quinolinium iodide



Suitably the reversible insolubiliser compound which is also a radiation absorbing compound constitutes at least 1%, preferably at least 2%, preferably up to 25%, more preferably up to 15%, of the total weight of the composition. Thus a preferred weight range for the reversible insolubiliser compound which is also a radiation absorbing compound may be expressed as 2-15% of the total weight of the composition.

The base which can be used as the support is preferably an aluminium plate which has undergone the usual anodic, graining and post-anodic treatments well known in the lithographic art for enabling a radiation sensitive composition to be coated thereon and for the surface of the support to function as a printing background.

Another base material which may be used in the method of the present invention is a plastics material base or a treated paper base as used in the photographic industry. A particularly useful plastics material base is polyethylene terephthalate which has been subbed to render its surface hydrophilic. Also a so-called resin coated paper which has been corona discharge treated can also be used.

Examples of lasers which can be used in the method of the present invention include semiconductor diode lasers emitting at between 600nm and 1100 nm. An example is the Nd YAG laser which emits at 1064nm, but any laser of sufficient imaging power (whose radiation is absorbed by the composition), can be used.

The compositions of the invention may contain other ingredients such as stabilising additives, inert colourants, additional inert polymeric binders as are present in many lithographic plate compositions.

Preferably the heat-sensitive compositions of the present invention do not comprise UV sensitive components. However, UV sensitive components which are not UV activated due to the presence of other components, such as inert UV absorbing dyes or a UV absorbing topmost layer, may be present.

Any feature of any aspect of the present invention or embodiment described herein may be combined with any feature of any other aspect of any invention or embodiment described herein.

The following Examples more particularly serve to illustrate the various aspects of the present invention described hereinabove.

The following products are referred to hereinafter:

Resin A: LB6564 - a phenol/cresol novolak resin marketed by Bakelite.

Resin B: R17620 - a phenol/formaldehyde resole resin marketed by B.P. Chemicals Ltd of Sully, Wales.

Resin C: SMD995 - an alkyl phenol/formaldehyde resole resin marketed by Schnectady Midland Ltd of Wolverhampton, England.

Resin D: Maruka Lyncur M(S-2) - a poly(hydroxystyrene) resin marketed by Maruzen Petrochemical Co. Ltd of Tokyo, Japan.

Resin E: Ronacoat 300 - a polymer based on dimethylmaleiimide marketed by Rohner Ltd of Pratteln, Switzerland.

Resin F: Gantrez An119 - a methylvinylether-co-maleic anhydride copolymer marketed by Gaf Chemicals Co., Guildford, England.

Resin G: SMA 2625P - a styrene maleic anhydride half ester marketed by Elf Atochem UK Ltd., Newbury, England.

Resin H: Cellulose acetate propionate (Mol. Wt. 75 000, containing 2.5% acetate and 45% to 49% propionate), marketed by Eastman Fine Chemicals, Rochester, USA.

Exposure Test Method

The coated substrate to be imaged was cut into a circle of 105mm diameter and placed on a disc that could be rotated at a constant speed between 100 and 2500 revolutions per minute. Adjacent to the spinning disc a translating table held the source of the laser beam so that the laser beam impinged normal to the coated substrate, while the translating table moved the laser beam radially in a linear fashion with respect to the spinning disc.

The laser used was a single mode 830nm wavelength 200mW laser diode which was focused to a 10 micron resolution. The laser power supply was a stabilised constant current source.

The exposed image was in the form of a spiral whereby the image in the centre of the spiral represented slow laser scanning speed and long exposure time and the outer edge of the spiral

represented fast scanning speed and short exposure time. Imaging energies were derived from the measurement of the diameter at which an image was formed.

The minimum energy that can be delivered by this exposure system is 150 mJ/cm^2 at an rpm of 2500.

Comparative Examples C1 to C5 and Examples 1 to 9

Coating formulations for all examples were prepared as solutions in 1-methoxypropan-2-ol with the exception of Examples 4, 5 and 8 which were prepared as solutions in 1-methoxypropan-2-ol/DMF 40:60 (v:v) and Example 7 as a solution in 1-methoxy propan-2-ol/DMF 35:65 (v:v). The substrate used was a 0.3 mm sheet of aluminium that had been electrograined and anodised and post-treated with an aqueous solution of an inorganic phosphate. The coating solutions were coated onto the substrate by means of a wire-wound bar. The solution concentrations were selected to provide the specified dry film compositions with a coating weight of 1.3 g per square metre after thorough drying at 100°C in an oven for 3 minutes.

	Comparative example				
	C1	C2	C3	C4	C5
Component	Parts by Weight				
Resin A	100	95.7	90	90	90
Dye B		4.25	4	4	4
Benzoic acid			6		
p-nitrophenol				6	
3',3",5',5"-tetrabromophenylphthalein					6

	Example								
	1	2	3	4	5	6	7	8	9
Component	Parts by Weight								
Resin A	86	90	90	90	90	90	90	90	90
Dye B	4	4	4	4	4	4	4	4	4
Dye A	10								
1-ethyl-4-methyl quinolinium bromide		6							
Monazoline C			6						
Benzothiazolium A				6					
Benzothiazolium B					6				
Cetyl pyridinium bromide						6			
Ethyl viologen dibromide							6		
Cetrimide								6	
Crystal Violet									6

Benzothiazoium A is 3-ethyl-2-[3-ethyl-2(3H) -benzothiazolylidene)-2-methyl-1-propenyl] benzothiazolium bromide.

Benzothiazoium B is 3-ethyl-2-methyl benzothiazolium iodide.

The plates were tested for developability by immersing in an aqueous developer solution for 30 seconds using an appropriate aqueous developer solution as described below.

Developer A:- 14% Sodium Metasilicate pentahydrate in water.

Developer B:- 7% Sodium Metasilicate pentahydrate in water.

The following table lists results of the simple developability tests for the compositions.

	Developer B
Comparative example	
1 to 5	Coating totally removed
Example	
1 to 9	No significant coating removal

The compositions described in the Comparative examples do not show resistance to developer attack. The compositions described in Examples 1 to 9 illustrate the effect of reducing the polymer developer solubility through the use of compounds described in the present invention.

Further samples of the plates were then imaged using the 830nm laser device described previously. The exposed discs were then processed by immersing in an aqueous developer solution for 30 seconds using an appropriate aqueous developer solution as described above. Plate sensitivities were then determined.

The results are listed in the following table.

	Developer A	Developer B
Comparative example		
1	No coating retained	
2	No coating retained	
3	No coating retained	
4	No coating retained	
5	No coating retained	
Example		
1		$\leq$ 150 mJ/cm^2
2	$\leq$ 150 mJ/cm^2	
3	$\leq$ 150 mJ/cm^2	
4	$\leq$ 150 mJ/cm^2	
5	$\leq$ 150 mJ/cm^2	
6	$\leq$ 150 mJ/cm^2	
7		$\leq$ 150 mJ/cm^2
8		$\leq$ 150 mJ/cm^2
9	$\leq$ 150 mJ/cm^2	

A printing plate made according to example 1 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

Example 10

A solution containing 8.15 g 1-methoxypropan-2-ol, 2.40 g of a 40% w/w solution Resin A in 1-methoxypropan-2-ol, 0.12 g of Dye A and 0.24 g of a Carbon black dispersion at 50% (w/w) in water was prepared and coated as described in Examples 1 to 9.

	Example 10
Component	Parts by Weight
Resin A	80
Dye A	10
Carbon Black	10

The resulting plate was imaged using a 200m W laser diode at a wavelength of 830nm using the imaging device described previously. The plate was then developed using Developer B for 30 seconds. The imaging energy density required to give a suitable image was ≤150mJ/cm^2.

A printing plate made according to example 10 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

Example 11

The plate precursor with the composition described in the following table was prepared as described for Example 4.

	Example 11
Component	Parts by Weight
Resin A	90
Dye D	10

The resulting plate was imaged using a 200m W laser diode at a wavelength of 830nm using the imaging device described previously. The plate was then developed using Developer B for 30 seconds. The imaging energy density required to give a suitable image was ≤150mJ/cm^2.

A printing plate made according to example 11 was also imaged on a commercially available image setter, the Trendsetter, supplied by Creo Products of Vancouver, Canada. The plate printed at least 10,000 good prints on a lithographic printing press.

Examples 12 -18

Coating formulations were prepared as previously described as solutions in 1-methoxy propan-2-ol with the exception of Example 16 which was prepared as a solution in 1-methoxy propan-2-ol/DMF 80:20 (v:v).

The formulations were coated as described in Examples 1 - 9 to provide dry film compositions as described in the following table.

	Example						
	12	13	14	15	16	17	18
Component	Parts by Weight						
Crystal Violet	6	6	6	6	6	6	6
Dye C	4	4	4	4	4	4	4
Resin A		45					
Resin B	90						
Resin C		45					
Resin D			90				
Resin E				90			
Resin F					90		
Resin G						90	
Resin H							90

Samples of the plates were then imaged using the 830nm laser device described previously. The exposed discs were then processed by immersing in a suitable aqueous developer solution, as described previously and below, for an appropriate time. Plate sensitivities were then determined. The results are listed in the following table.

Developer C:- 15% β–naphthylethoxylate, 5% benzyl alcohol, 2% nitrilo-triacetic acid trisodium salt, 78% water.

Developer D:- 3% β–naphthylethoxylate, 1% benzyl alcohol, 2% nitrilo-triacetic acid trisodium salt, 94% water.

Developer E:- 1.5% β–naphthylethoxylate, 0.5% benzyl alcohol, 1% nitrilo-triacetic acid trisodium salt, 97% water.

	Developer	Time / seconds	Sensitivity
Example			
12	B	90	248 mJ/cm^2
13	A	90	277 mJ/cm^2
14	C	45	277 mJ/cm^2
15	D	5	253 mJ/cm^2
16	E	60	461 mJ/cm^2
17	D	90	300 mJ/cm^2
18	A	120	700 mJ/cm^2

Examples 19-30

Coating formulations were prepared as previously described as solutions in 1-methoxy propan-2-ol with the exception of example 26 which was prepared as a solution in 1-methoxy propan-2-ol/DMF 50:50 (v:v).

The formulations were coated as described in Examples 1-9 to provide dry film compositions as described in the following table.

	Example											
	19	20	21	22	23	24	25	26	27	28	29	30
Component	Parts by Weight											
Dye B	4	4	4	4	4	4	4	4				
Dye C									4	4	4	4
Resin A	90	90	90	90	90	90	90	90	90	90	90	90
α-Naphthoflavone	6											
β-Naphthoflavone		6										
Flavone			6									
Xanthone				6								
Flavanone					6							
Benzophenone						6						
2,3-Diphenyl-1-indeneone							6					
N-(4-bromobutyl) phthalimide								6				
Phenanthrene quinone									6			
Acridine Orange Base (CI solvent orange 15)										6		
p-Toluene sulfonyl chloride											6	
Ethyl-p-toluene sulfonate												6

Samples of the plates were then imaged using the 830nm laser device described previously. The exposed discs were then processed by immersing in a suitable aqueous developer

solution, for an appropriate time. Plate sensitivities were then determined. The results are listed in the following table.

	Developer	Time / seconds	Sensitivity
Example			
19	A	30	$\leq$ 150 mJ/cm^2
20	A	30	$\leq$ 150 mJ/cm^2
21	A	30	290 mJ/cm^2
22	A	30	$\leq$ 150 mJ/cm^2
23	A	30	$\leq$ 150 mJ/cm^2
24	B	30	220 mJ/cm^2
25	B	30	$\leq$ 150 mJ/cm^2
26	B	15	$\leq$ 150 mJ/cm^2
27	B	60	250 mJ/cm^2
28	A	90	250 mJ/cm^2
29	B	10	400 mJ/cm^2
30	B	60	250 mJ/cm^2

Example 31

The coating formulation was prepared as previously described as a solution in 1-methoxy propan-2-ol. The formulation was coated as described in examples 1-9 to provide a dry film composition as described in the following table.

	Example 31
Component	Parts by Weight
Resin A	90
Dye C	4
Crystal Violet	6

Samples of the plate were subjected to heat delivered from a Weller Soldering Iron EC 2100 M at 311°C. The speed of movement of the soldering iron over the plate surface is

described in the table below. The exposed plate samples were then processed by immersion in developer A for 60 seconds. The results are listed in the table below.

Speed of Soldering Iron Movement over Plate Surface / cm s^{-1}	Heat applied to..	Simple Developability Test Result
1	coated face of plate	Coating totally removed in area subjected to heat
10	coated face of plate	Coating totally removed in area subjected to heat
20	coated face of plate	Coating totally removed in area subjected to heat
50	coated face of plate	Coating totally removed in area subjected to heat
1	reverse face of plate, i.e. direct on the aluminium support	Coating totally removed in area subjected to heat
10	reverse face of plate, i.e. direct on the aluminium support	Coating totally removed in area subjected to heat

In the specification, we refer in various places to UV light. A person skilled in the art will be aware of the typical wavelength range of UV light. However, for the avoidance of any doubt, UV typically has a wavelength range of 190 nm to 400 nm.

All of the features disclosed in this specification (including any accompanying claims, abstract and drawings), and/or all of the steps of any method or process disclosed, may be combined in any combination, except combinations where at least some of such features and/or steps are mutually exclusive.

Each feature disclosed in this specification (including any accompanying claims, abstract and drawings), may be replaced by alternative features serving the same, or equivalent or similar purpose, unless expressly stated otherwise. Thus, unless expressly stated otherwise, each feature disclosed is one example only of a generic series of equivalent or similar features.

The invention is not restricted to the details of the foregoing embodiment(s). The invention extends to any novel one, or any novel combination, of the features disclosed in this

specification (including any accompanying claims, abstract and drawings), or to any novel one, or any novel combination, of the steps of any method or process so disclosed.

Claims:-

1. An oleophilic, heat-sensitive composition comprising an aqueous developer soluble polymeric substance and a compound which reduces the aqueous developer solubility of the polymeric substance characterised in that the aqueous developer solubility of the composition is increased on heating and that the aqueous developer solubility of the composition is not increased by incident UV radiation.

2. A composition as claimed in claim 1 wherein the aqueous developer soluble polymeric substance comprises a functional group or groups selected from hydroxy, carboxylic acid, amino, amide and maleiimide.

3. A composition as claimed in claim 1 wherein the aqueous developer soluble polymeric substance is selected from a polymer or copolymer of hydroxystyrene, a polymer or copolymer of acrylic acid, a polymer or copolymer of methacrylic acid, a polymer or copolymer of maleiimide, a polymer or copolymer of maleic anhydride, a hydroxycellulose, a carboxy cellulose and a phenolic resin.

4. A composition as claimed in claim 1 wherein the aqueous developer soluble polymeric substance is a phenolic resin.

5. A composition as claimed in claim 4 wherein the aqueous developer solution is an aqueous alkaline solution.

6. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a compound which comprises at least one nitrogen atom which is quarternised.

7. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a compound which comprises at least one nitrogen atom incorporated in a heterocyclic ring.

8. A composition as claimed in claim 7 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from a quinoline and a triazole.

9. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a compound which comprises at least one quarternised nitrogen atom incorporated in a heterocyclic ring.

10. A composition as claimed in claim 9 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from a imidazoline compound, a quinolinium compound, a benzothiazolium compound and a pyridinium compound.

11. A composition as claimed in claim 10 wherein the quinolinium compound is a cyanine dye.

12. A composition as claimed in claim 10 wherein the benzothiazolium compound is a cyanine dye.

13. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a triarylmethane compound.

14. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a compound which comprises a carbonyl functional group.

15. A composition as claimed in claim 14 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from a flavone compound.

16. A composition as claimed in claim 14 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from flavanone, xanthone, benzophenone, N-(4-bromobutyl)phthalimide, 2,3-diphenyl-1-indeneone and phenanthrenequinone.

17. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a compound of general formula:

$$Q_1\text{-}S(O)_n\text{-}Q_2$$

Where Q_1 represents an optionally substituted phenyl or alkyl group, n represents 0, 1 or 2, and Q_2 represents a halogen atom or an alkoxy group.

18. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is selected from ethyl-p-toluene sulfonate and p-toluenesulfonyl chloride.

19. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is acridine orange base (CI solvent orange 15).

20. A composition as claimed in claim 1 wherein the compound which reduces the aqueous developer solubility of the polymeric substance is a ferrocenium compound.

21. A positive working lithographic printing form precursor having a coating comprising of a composition as claimed in any preceding claim coated on a support having a hydrophilic surface.

22. A lithographic printing form precursor as claimed in claim 21 wherein said coating is suitably adapted to preferentially absorb radiation and convert said radiation to heat.

23. A lithographic printing form precursor as claimed in claim 22 wherein said composition comprises a radiation absorbing compound capable of absorbing incident radiation and converting it to heat.

24. A lithographic printing form precursor as claimed in claim 22 wherein said coating comprises an additional layer disposed beneath the composition as claimed in claim 1 wherein the additional layer comprises a radiation absorbing compound capable of absorbing incident radiation and converting it to heat.

25. A lithographic printing form precursor as claimed in claim 22 wherein the compound which reduces the aqueous developer solubility of the polymeric substance of the composition as claimed in claim 1 is also a radiation absorbing compound capable of absorbing incident radiation and converting it to heat.

26. A lithographic printing form precursor as claimed in claims 23 and 24 wherein the radiation absorbing compound is carbon black.

27. A lithographic printing form precursor as claimed in claims 23 and 24 wherein the radiation absorbing compound is a pigment.

28. A lithographic printing form precursor as claimed in claim 27 wherein the pigment is an organic pigment.

29. A lithographic printing form precursor as claimed in claim 28 wherein the pigment is a phthalocyanine pigment.

30. A lithographic printing form precursor as claimed in claim 27 wherein the pigment is an inorganic pigment.

31. A lithographic printing form precursor as claimed in claim 27 wherein the pigment is selected from Prussian Blue, Heliogen Green or Nigrosine.

32. A lithographic printing form precursor as claimed in claims 23 and 24 wherein the radiation absorbing compound is a dye selected from one of the following classes, squarylium, merocyanine, cyanine, indolizine, pyrylium or metal dithioline.

33. A lithographic printing form precursor as claimed in claim 24 wherein the separate radiation absorbing layer is a thin layer of dye or pigment.

34. A lithographic printing form precursor as claimed in claim 24 wherein the separate radiation absorbing layer is a thin layer of metal or metal oxide.

35. A lithographic printing form precursor as claimed in claim 25 wherein the compound which reduces the aqueous developer solubility of the polymeric substance and is also a radiation absorbing compound is a cyanine dye which comprises a quinolinium moiety.

36. A lithographic printing form precursor as claimed in claims 27, 32 and 35 wherein the radiation absorbing compound absorbs at above 600nm.

37. A method for producing a lithographic printing form comprising direct imagewise application of radiation to a precursor described in any preceding claim.

38. A method as claimed in claim 37 wherein the radiation is delivered from a laser.

39. A method as claimed in claim 38 wherein the laser emits radiation at above 600nm.

40. A method as claimed in claim 27 wherein the heat is delivered from a heated body.

41. An imaged printing form produced by application of a method as claimed in any of claims 37 to 40 to a printing form precursor as claimed in any of claims 21 to 36.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 97/01117

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 B41C1/10 B41M5/36

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 6 B41C B41M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 708 925 A (NEWMAN STEPHEN) 24 November 1987 cited in the application see example 35 ---	1
X	GB 1 245 924 A (AGFA-GEVAERT) 15 September 1971 cited in the application see examples 3,28 ---	1,37
X	DE 19 15 273 A (AGFA-GEVAERT) 2 October 1969 see examples 3,4 ---	1,37
X	EP 0 631 189 A (AGFA GEVAERT NV) 28 December 1994 see page 6, line 7 - line 13 --- -/--	1,37

[X] Further documents are listed in the continuation of box C.

[X] Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

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Date of the actual completion of the international search	Date of mailing of the international search report
4 September 1997	24.09.97
Name and mailing address of the ISA European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Tx. 31 651 epo nl, Fax: (+31-70) 340-3016	Authorized officer Heywood, C

Form PCT/ISA/210 (second sheet) (July 1992)

INTERNATIONAL SEARCH REPORT

Internatio Application No
PCT/GB 97/01117

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 0 652 483 A (MINNESOTA MINING & MFG) 10 May 1995 cited in the application see the whole document ---	1-41
A	US 5 491 046 A (DEBOER CHARLES D ET AL) 13 February 1996 cited in the application see the whole document ---	1-41
A	US 5 372 907 A (HALEY NEIL F ET AL) 13 December 1994 cited in the application see the whole document ---	1-41
A	GB 2 082 339 A (HORSELL GRAPHIC IND LTD) 3 March 1982 cited in the application see the whole document -----	1-41

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